New particle formation observed in the tropical/subtropical cirrus clouds

S.-H. Lee,[1] J. C. Wilson,[1] D. Baumgardner,[2,3] R. L. Herman,[4] E. M. Weinstock,[5] B. G. LaFleur,[1,6] G. Kok,[2] B. Anderson,[7] P. Lawson,[8] B. Baker,[8] A. Strawa,[9] J. V. Pittman,[5] J. M. Reeves,[1] and T. P. Bui[9]

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[1] Previous studies show that new particle formation takes place in the outflows of marine stratus and cumulus clouds. Here we show measurements of high concentrations of ultrafine particles, diameters (D_p) from 4 to 9 nm (N_{4-9}), in interstitial cloud aerosol. These ultrafine particles indicate that in situ new particle formation occurs interstitially in cirrus clouds. Measurements were made at altitudes from 7 to 16 km over Florida with instruments on the WB-57F aircraft during Cirrus Regional Study of Tropical Anvils and Cirrus Layers-Florida Area Cirrus Experiments (CRYSTAL-FACE) in July 2002. Size-resolved ice crystal particle concentrations and water vapor concentrations were measured to help identify the presence of cirrus clouds. About 72% of the in-cloud samples showed new particle formation events with the average N_{4-9} of 3.0×10^3 cm^{-3}, whereas about 56% of the out-of-cloud samples had events with the lower N_{4-9} of 1.3×10^3 cm^{-3}. The periods during which high N_{4-9} appeared were often associated with times of increasing ice water content (IWC) and high relative humidity with respect to ice (RHI); however, the measured N_{4-9} was not quantitatively correlated to IWC. The magnitude and frequency of new particle formation events seen in cirrus clouds were also higher than those previously observed in the tropical/subtropical upper troposphere in the absence of clouds. These results suggest that cirrus clouds may provide favorable conditions for particle formation, such as low temperatures, high RHI, high OH production (due to high water vapor), cloud electricity, and atmospheric convection. At present, however, particle formation mechanisms in clouds are unidentified. *INDEX TERMS:* 0305 Atmospheric Composition and Structure: Aerosols and particles (0345, 4801); 0320 Atmospheric Composition and Structure: Cloud physics and chemistry; 0335 Atmospheric Composition and Structure: Ion chemistry of the atmosphere (2419, 2427); 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry; 0368 Atmospheric Composition and Structure: Troposphere—constituent transport and chemistry; *KEYWORDS:* new particle formation, cirrus clouds, upper troposphere and lower stratosphere (UT-LS)

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1. Introduction

[2] The upper troposphere and lower stratosphere (UT-LS) are a source of new particles [*Brock et al.*, 1995; *Schröder and Ström*, 1997; *de Reus et al.*, 1999; *Nyeki et al.*, 1999; *Wang et al.*, 2000; *Hermann et al.*, 2003; *Lee et al.*, 2003] because of several factors favorable for particle nucleation, such as low temperatures and relatively low surface area of preexisting aerosol. New particles are formed under the typical UT-LS conditions of SO_2 concentrations, temperature, and relative humidity with respect to ice (RHI), with sufficient Sun exposure and low preexisting aerosol surface area [*Lee et al.*, 2003]. Because these newly formed particles may grow to cloud condensation nuclei (CCN) (diameter $D_p > \sim 50$ nm), they play an important role in cloud formation and hence have an impact on global and regional climate.

[3] Several different nucleation processes have been used to explain atmospheric particle formation, including binary homogeneous nucleation (BHN) of sulfuric acid–

[1]Department of Engineering, University of Denver, Denver, Colorado, USA.
[2]Droplet Measurement Technologies, Boulder, Colorado, USA.
[3]Centro de Ciencias de la Atmosfera, Universidad Nacional Autonoma de Mexico, Mexico City, Mexico.
[4]Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California, USA.
[5]Engineering and Applied Sciences, Harvard University, Cambridge, Massachusetts, USA.
[6]Now at Climate Modeling and Diagnostics Laboratory, National Oceanic and Atmospheric Administration, Boulder, Colorado, and Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder, Colorado, USA.
[7]Chemistry and Dynamics Branch, NASA Langley Research Center, Hampton, Virginia, USA.
[8]SPEC, Inc., Boulder, Colorado, USA.
[9]NASA Ames Research Center, Moffett Field, California, USA.

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water (H_2SO_4-H_2O) [e.g., *Seinfeld and Pandis*, 1997; *Vehkamäki et al.*, 2002], ternary homogeneous nucleation (THN) of sulfuric acid–ammonia–water (H_2SO_4-NH_3-H_2O) [*Kulmala et al.*, 2000; *O'Dowd et al.*, 2002], and ion-induced nucleation (IIN) [*Yu and Turco*, 2001; *Laakso et al.*, 2002; *Lee et al.*, 2003; *Lovejoy et al.*, 2004]. At present, however, it is unclear which nucleation process dominates in the atmosphere [*Kulmala*, 2003]. BHN has been widely used to explain new particle formation, but it was often found that the measured particle concentrations exceed those predicted. In THN, ammonia (or other condensable organic species) acts to stabilize the critical embryo by decreasing the vapor pressure of sulfuric acid, resulting in higher nucleation rates than BHN. IIN involves ion clusters that form by electrons initially produced by cosmic rays and by the subsequent sequence of chain reactions of atmospheric ions [e.g., *Viggiano and Arnold*, 1995]. These electrically charged clusters are much more stable and grow faster than neutral species. Ion production rates are highest at altitudes from 10 to 14 km [*Beig and Brasseur*, 2000], and IIN may play an important role in the UT-LS [*Lee et al.*, 2003; *Lovejoy et al.*, 2004].

[4] Compared with the midlatitude and high-latitude UT-LS, the tropical/subtropical UT region has additional factors favorable for particle nucleation, such as higher concentrations of SO_2, condensable organic species, and ammonia, as well as longer Sun exposure hours all year (hence higher OH concentrations). It has also been suggested that atmospheric mixing processes, such as vertical dynamic mixing and the Intertropical Convergence Zone, can enhance nucleation rates [e.g., *Schröder and Ström*, 1997; *de Reus et al.*, 1999; *Hermann et al.*, 2003]. This may be because (1) temperature and RHI fluctuations in two mixed air masses can enhance BHN rates [*Easter and Peters*, 1993], (2) atmospheric convection can bring higher concentrations of SO_2 to the higher altitudes, and (3) saturation vapor pressures of H_2SO_4 may be reduced in mixed air parcels [*Nilsson and Kulmala*, 1998]. Moreover, previous measurements have shown that marine stratus and cumulus clouds provide an environment where new particle formation may occur easily [e.g., *Radke and Hobbs*, 1991; *Hoppel et al.*, 1994; *Weidensohler et al.*, 1996; *Clarke et al.*, 1998, 1999] because cloud processing lowers the surface area of preexisting aerosol and provides higher RHI. Preexisting aerosol surface area is the sink for newly formed particles, since in the presence of a large surface area, H_2SO_4 vapors effectively condense on, and small particles coagulate with, the preexisting aerosol particles. However, at present it has not been examined how the cirrus clouds produced in convective outflow and anvil dissipation in the tropics/subtropics affect particle nucleation.

[5] Here we report the size-resolved aerosol particle concentrations, covering the D_p range from 4 to 2000 nm, measured in the tropical/subtropical UT. We also use the derived ice water content (IWC) from measured ice crystal particles with D_p from 0.5 to 1600 μm and water vapor to characterize cirrus clouds.

2. Experiments

[6] The objectives of the Cirrus Regional Study of Tropical Anvils and Cirrus Layers-Florida Area Cirrus Experiments (CRYSTAL-FACE) mission are described by *Jensen et al.* [2004]. Characterization of the instruments used in CRYSTAL-FACE is given at the project Web site, http://cloud1.arc.nasa.gov/crystalface/instruments.html. The University of Denver Nucleation-Mode Aerosol Sizing Spectrometer (N-MASS) [*Brock et al.*, 2000] and the Focused Cavity Aerosol Spectrometer (FCAS) [*Jonsson et al.*, 1995] were used to measure size distributions with D_p from 4 to 100 nm and 90 to 2000 nm, respectively. Both N-MASS and FCAS use the passive, near-isokinetic sampling inlet [*Jonsson et al.*, 1995]. In the FCAS the sample flow is passed through a laser beam, and the light scattered by individual particles is measured. Particle size is related to the scattered light on the basis of Mie theory and calibrations with known particles. Water is evaporated from particles during sampling and transport to the laser. We show here the size distributions of these dried particles. Calculations show that sulfuric acid and water particles in the size range detected by the FCAS would lose most of their water prior to measurement. Assuming the particles to be sulfuric acid and water, ambient size distributions can be constructed from the dry sizes and the measured water vapor and temperature. Within the N-MASS instrument the sample flow is carried to five parallel condensation nucleus counters (CNCs) operated at 60 hPa pressure. The supersaturation in each CNC is tuned to measure the cumulative concentration of particles larger than a given diameter, D_{50}, for which 50% of the particles are detected. The values of D_{50} for the five CNCs are 4.0, 7.5, 15, 30, and 55 nm, respectively. By combining the N-MASS and FCAS measurements and by using an inversion program based on the nonlinear technique of *Markowski* [1988], particle sizes and concentrations are determined for particles with D_p from 4 to 2000 nm. The concentrations of particles with D_p from 4 to 9 nm are further derived from the size distributions. The inversion technique makes use of the full response matrix of each instrument. In the case of the N-MASS the response matrix consists of the fraction of particles counted by each CNC for nearly monodisperse test aerosols. The FCAS response matrix describes the distribution of pulse heights resulting from measurements of monodisperse test aerosols and the fraction of particles of each size that are detected. The test aerosols cover the size ranges of each instrument. The data reduction and inversion also include corrections for diffusion loss and departures from isokinetic sampling in the inlet.

[7] We use the following two criteria to quantitatively examine the feature of new particle formation: (1) N_{4-9} is higher than 1 cm^{-3}, and (2) the particle numbers with D_p from 4 to 6 nm (N_{4-6}) are higher than those with D_p from 6 to 9 nm (N_{6-9}). This lower limit of N_{4-9} is set by considering the high-altitude polar regions where the total aerosol concentrations with D_p from 4 to 2000 nm (N_{4-2000}) are only ~15 cm^{-3}; during CRYSTAL-FACE, all measurements satisfied the first criterion. Although we do not know well about the shape of size distributions between 4 and 9 nm from the N-MASS measurements, by using the second criterion, we can assure that there are more particles in the range from 4 to 9 nm than between 9 and 15 nm.

[8] The forward-facing inlet cannot discriminate between aerosol and ice particles. Artifacts arising from the sampling of ice particles that shatter or do not completely evaporate in

Table 1. Aerosol Particle and Cirrus Ice Crystal Concentrations Measured During CRYSTAL-FACE at Potential Temperatures From 330 to 430 K for the In-Cloud and Out-of-Cloud Samples[a]

Date	Ice Crystal Number D_p 0.5–1600 μm, cm^{-3}	Ice Crystal Surface D_p 0.5–1600 μm, $\mu m^2\ cm^{-3}$	IWC D_p 0.5–1600 μm, $g\ m^{-3}$	N_{4-9} D_p 4–9 nm, cm^{-3}	N_{4-2000} D_p 4–2000, cm^{-3}
			In-Cloud Samples		
7 July 2002	1.7×10^2	1.3×10^3	4.7×10^{-2}	2.2×10^3	2.5×10^3
11 July 2002	1.8×10^0	6.5×10^2	1.2×10^{-2}	5.4×10^3	6.6×10^3
19 July 2002	6.8×10^0	3.0×10^3	3.4×10^{-2}	7.7×10^2	2.6×10^3
23 July 2003	6.3×10^0	9.5×10^2	1.0×10^{-2}	4.6×10^3	6.8×10^3
26 July 2003	1.1×10^0	2.9×10^2	2.1×10^{-3}	1.4×10^4	1.5×10^4
28 July 2003	6.3×10^0	3.3×10^3	5.2×10^{-2}	8.0×10^2	1.3×10^3
Average	2.7×10^1	1.2×10^3	2.1×10^{-2}	4.2×10^3	5.1×10^3
			Out-of-Cloud Samples		
7 July 2002	2.8×10^{-2}	5.0×10^{-2}	7.7×10^{-8}	7.0×10^2	7.4×10^2
11 July 2002	5.1×10^{-1}	5.6×10^{-1}	5.6×10^{-8}	4.5×10^2	5.4×10^2
19 July 2002	1.1×10^{-1}	1.4×10^{-1}	6.4×10^{-8}	1.7×10^2	4.8×10^2
23 July 2002	2.3×10^{-1}	2.8×10^{-1}	8.9×10^{-8}	4.8×10^1	2.0×10^2
26 July 2002	4.3×10^{-1}	4.8×10^{-1}	6.2×10^{-8}	8.1×10^2	1.1×10^3
28 July 2002	7.5×10^{-2}	1.0×10^{-1}	7.0×10^{-8}	3.8×10^2	6.0×10^2
Average	1.6×10^{-2}	1.9×10^{-1}	5.6×10^{-8}	4.6×10^2	5.6×10^2

[a]In-cloud samples were selected when RHI > 95% and IWC > 1.0×10^{-4} g m^{-3}, and the out-of-cloud samples were selected when RHI < 80% and IWC < 1.0×10^{-5} g m^{-3}.

transport to the instruments are possible. The measurements in cloud include mostly interstitial aerosol and some cloud particles. However, as shown in section 3, contribution from clouds to the aerosol number concentrations was small, but the aerosol surface area and volume concentrations were affected by ice crystals that arrived at the laser in partially evaporated form. Chemical analysis of particles sampled through a similar inlet also revealed some contamination [*Kojima et al.*, 2004]. Artifact effects of cirrus clouds occurring in the aircraft aerosol sampling inlet are described by *Murphy et al.* [2004].

[9] Ice crystal particle concentrations with D_p from 0.5 to 1600 μm were derived from the combined size spectra measurements made by the Droplet Measurement Technologies, Inc. cloud, aerosol, and precipitation spectrometer (CAPS), the modified SPP-100 scattering spectrometer (SPP), and the SPEC, Inc. cloud particle imager (CPI). The CAPS measures particles with D_p from 0.5 to 44 μm and 75 to 1600 μm [*Baumgardner et al.*, 2002], SPP measures from 4 to 57 μm, and CPI measures from 10 to 300 μm. The measurements from the three instruments were combined to form a composite size distribution from which IWC was derived using the integrated volume concentrations.

[10] Water vapor mixing ratios were measured by two different instruments: the Jet Propulsion Laboratory laser hygrometer [*May*, 1998] and the Harvard water vapor photofragment fluorescence hygrometer [*Weinstock et al.*, 1994]. These two water measurements agreed with each other to within ~10%. Temperature was measured by the NASA Ames Research Center Meteorological Measuring System [*Scott et al.*, 1990]. We used the average of the two water vapor measurements and MMS temperature measurement to determine RHI.

3. Results

[11] The IWC derived from ice crystal concentrations with D_p from 0.5 to 1600 μm and the ice crystal numbers with D_p from 3 to 1600 μm showed, on average, a similar trend during the mission (although the ice crystal numbers were dominated by the smaller-size particles with D_p < 60 μm). Hence the contribution of background aerosol particles (D_p < 3 μm) to the estimated IWC was negligible. For IWC greater than 1.0×10^{-4} g m^{-3} the average RHI was 114 ± 21% (1σ), and for IWC less than 1.0×10^{-5} g m^{-3} the RHI was 57 ± 37%. We selected the in-cloud-samples when RHI >95% and IWC > 1.0×10^{-4} g m^{-3} and the out-of-cloud samples when RHI < 80% and IWC < 1.0×10^{-5} g m^{-3}. These criteria excluded a small number of observations of clouds at low RHI and of clear air at high RHI. For the in-cloud samples satisfying the above criteria, the average surface area of ice crystal particles, assuming that the particles are spherical, was >1.0×10^2 $\mu m^2\ cm^{-3}$ (Table 1), which was the same as the cloud identification used in other CRYSTAL-FACE studies [e.g., *Gao et al.*, 2004].

[12] Figure 1 shows the time variation of temperature, RHI, N_{4-9}, and IWC measured on 23 July 2002. There were several instances where high N_{4-9} clearly coincided with the periods of high IWC and RHI. Although the occurrence of a high N_{4-9} was closely related to the presence of cloud particles (Figure 1), the amount of N_{4-9} was not quantitatively correlated to the IWC or to the number concentration of ice crystals (Table 1 and Figure 2). These results suggest new particle formation in cirrus clouds.

[13] Vertical distribution of N_{4-9} showed that most of the cloud particle observations made from the WB-57F occurred at potential temperatures from ~340 to ~360 K (or altitudes from ~13 to ~16 km) (Figure 3a). On the other hand, new particle formation events seen outside of clouds took place at all altitude ranges, at potential temperatures from ~330 to ~430 K, and with strong altitude dependence (Figure 3a), consistent with our previous measurements in the UT-LS [*Lee et al.*, 2003]. We thus contrast measurements of aerosol made outside of clouds with those made in the presence of cloud particles in the same range of potential temperatures as the cloud measurements.

[14] New particle formation in cirrus clouds was further illustrated by the aerosol size distributions with D_p from 4 to

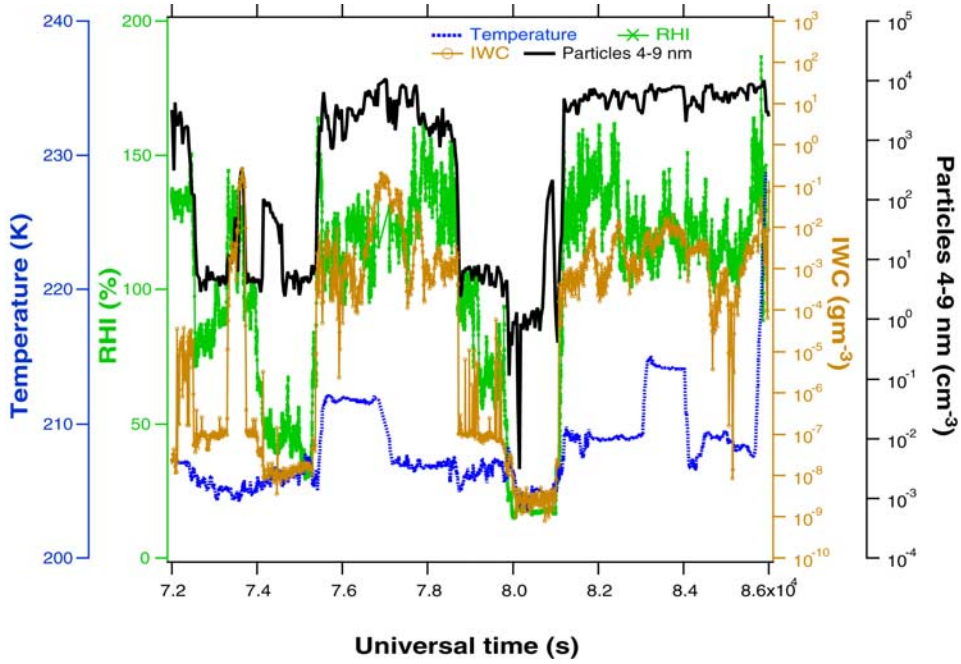

Figure 1. Measured temperature (blue), RHI (green), IWC (orange), and N_{4-9} (black) on 23 July 2002 during CRYSTAL-FACE as a function of universal standard time. Temperature and RHI are 1-s averages, IWC is a 10-s average, and N_{4-9} is a 30-s average.

2000 nm for the in- and out-of-cloud samples (Figure 3b). The median N_{4-9} in clouds with new particle formation events was 3.0×10^3 cm^{-3}, higher than that in clear air, 1.3×10^3 cm^{-3} (Table 2). Both of these size distributions show a high peak at $D_p < 10$ nm and another peak at $D_p \sim 20$ nm. About 72% of the in-cloud samples experienced new particle formation events compared with about 56% of the out-of-cloud samples that had events, suggesting that cirrus clouds provide a favorable condition for new particle formation. N_{4-2000} measured at cirrus cloud levels fell between 1.0×10^2 and 3.0×10^4 cm^{-3}, with higher concentrations in clouds than outside of clouds. In clouds, even without new particle events, a substantially high N_{4-2000} of 7.4×10^3 cm^{-3} was observed with a maximum at $D_p \sim 20$ nm (Figure 3b and Table 2). These particles have a strong potential to grow to CCN sizes.

[15] The high number of particle concentrations from the in-cloud samples may be a result of shattering by large ice crystal particles in the sampling inlet. We tested this possibility in three ways by using the measured aerosol particle concentrations and size distributions. First, high N_{4-9} was measured with high IWC in clouds, but the amounts of N_{4-9} were not quantitatively correlated to the number of ice crystals or IWC (Table 1 and Figure 2). For example, with high IWC the measured N_{4-9} was sometimes remarkably lower than in the case of low IWC (Table 1). Second, ultrafine particles were also observed without high IWC in clear air, clear evidence that measured ultrafine particles were not necessarily the artifact of ice crystals. We note that the size distributions characterizing new particle formation in and out of clouds were very similar in shape (Figure 3b), which suggests that collisions of ice crystals in the inlet are not likely creating ultrafine particles. Third, the aerosol numbers with D_p from 90 to 2000 nm (FCAS number concentrations) varied by less than a factor of 2 when comparing the in- and out-of-cloud samples (not shown). These results suggest that our sampling inlet had sampled some ice crystal particles at high RHI, but they have not affected our number size distributions; otherwise, number concentrations with D_p from 90 to 2000 nm would have been very different for the in- and out-of-cloud

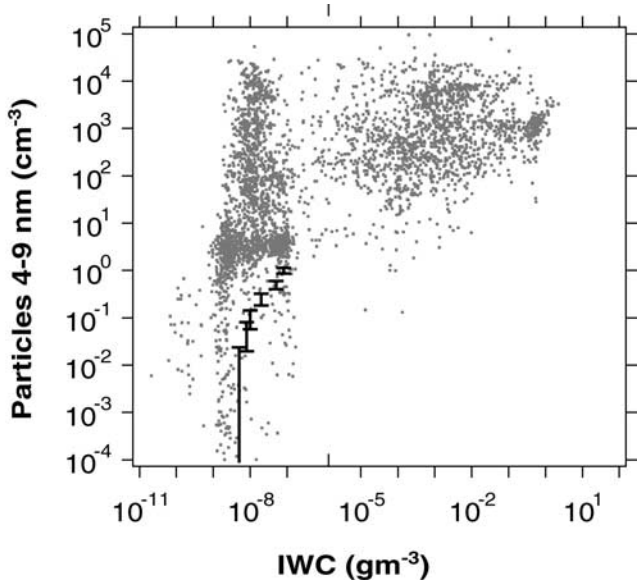

Figure 2. Measured N_{4-9} as a function of IWC for all CRYSTAL-FACE samples measured at potential temperatures from 330 to 430 K. The uncertainties (vertical bars) in statistical counting of N-MASS are taken from *Lee et al.* [2003].

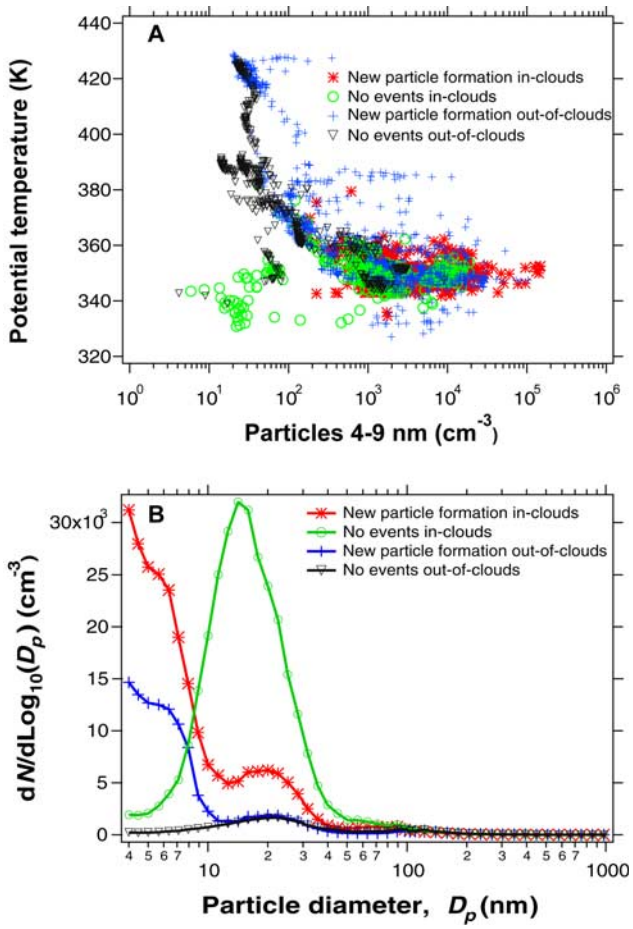

Figure 3. Altitude dependence of (a) N_{4-9} and (b) average size distributions for aerosol particles with D_p from 4 to 2000 nm, measured during CRYSTAL-FACE at potential temperatures from 340 to 360 K for the in-cloud samples with (red) and without (green) new particle formation events and for the out-of-cloud samples with (blue) and without (black) events.

samples. On the other hand, the volume concentrations of total background aerosols increased with RHI for both in- and out-of-cloud samples (not shown). The particle size distributions for surface area and volume also showed that the aerosol volume and surface concentrations were affected. *Hegg et al.* [1990] have also shown that the interfering contribution from cloud droplets to the condensation nuclei (CN) number concentration is small on the basis of their cloud measurements and the previous laboratory experiments of droplet evaporations [*Radke and Hobbs*, 1972], although some disagreements exist [e.g., *Saxena and Hendler*, 1983; *Hudson and Frisbie*, 1991].

4. Discussion

[16] While this study focuses on the new particle formation in clouds, we have also observed numerous cases of high N_{4-9} from the out-of-cloud samples (Figures 2 and 3). These incidents are representative of the background level of new particle formation events and are also consistent with the previous measurements in the tropics/subtropics during the WB-57F Aerosol Mission (WAM) and Atmospheric Chemistry of Combustion Aerosol Missions Near the Tropopause (ACCENT) [*Lee et al.*, 2003]. New particle formation has a strong latitude and altitude dependence in the UT-LS: higher magnitude and frequency at lower latitudes and lower altitudes than at higher latitudes and higher altitudes [*Lee et al.*, 2003]. Hence, even without cloud events, particle formation is expected to occur in the tropical/subtropical UT. However, the frequency and amplitude of new particle formation observed in the cirrus clouds were much higher compared with the cases in the absence of clouds. During WAM and ACCENT, ~20% of the background tropical/subtropical samples showed the feature of new particle formation with average N_{4-9} of ~1.1 × 10^3 cm^{-3}; these samples excluded those influenced by rocket plumes or clouds (by choosing RHI < 95%). In contrast, during CRYSTAL-FACE, overall, ~40% of the samples had the feature of new particle formation, with an average N_{4-9} of 5.8 × 10^3 cm^{-3}, when considering all measurement altitudes.

[17] The appearance of high ultrafine particles signifies recent formation of new particles. These particles were seen clearly over the same relative humidity ranges as ice crystals. One can expect that new particles are more likely to be formed at higher humidities, and the presence of crystals is certainly a marker for air in which the humidity recently reached saturation with respect to ice. Previous measurements of condensation nuclei near marine clouds have also suggested that the enhanced relative humidity is a key factor for new particles near clouds [e.g., *Hegg et al.*, 1990; *Hoppel et al.*, 1994; *Clarke et al.*, 1999]. This is because the nucleation rates are more sensitive to relative

Table 2. Median Aerosol Particle and Cirrus Ice Crystal Concentrations Acquired in CRYSTAL-FACE at Potential Temperatures From 340 to 360 K, With New Particle Formation Events In and Out of Clouds and Without Events In and Out of Clouds

	Ice Crystal Number D_p 0.5–1600 μm, cm^{-3}	Ice Crystal Surface D_p 0.5–1600 μm, μm^2 cm^{-3}	IWC D_p 0.5–1600 μm, g m^{-3}	N_{4-9} D_p 4–9 nm, cm^{-3}	N_{4-2000} D_p 4–2000, cm^{-3}
			In Clouds		
Events	1.5×10^0	5.2×10^2	3.8×10^{-3}	3.0×10^3	4.4×10^3
No events	1.2×10^0	3.9×10^2	2.6×10^{-3}	5.6×10^2	7.4×10^3
			Out of Clouds		
Events	9.0×10^{-2}	1.0×10^{-1}	1.3×10^{-8}	1.3×10^3	2.2×10^3
No events	9.0×10^{-2}	1.0×10^{-2}	1.0×10^{-8}	3.6×10^1	2.9×10^2

humidity, while condensation of H_2SO_4 vapors on aerosol particles varies less dramatically over a large range of relative humidity.

[18] Clouds scavenge aerosol particles, leading to a reduction in the surface area of an air mass, and enhance particle nucleation and growth in the outflow of clouds. However, we have measured high concentrations of ultrafine particles from the cloud interstitial samples, where the surface areas of ice crystal particles were very high, $>1.0 \times 10^2$ μm^2 cm^{-3} (Table 1). Observations of new particle formation in clouds are scarce. *Hoppel et al.* [1994] have reported interstitial aerosol size distributions that are indicative of new particle formation within stratus clouds, coexisting with high concentrations of cloud droplet surface area, in the clean marine boundary layer (hence low SO_2). Other observations have also shown high CN concentrations associated with marine cumulus clouds [*Hegg et al.*, 1990, 1991]. J. R. Peter et al. (Prediction and observation of aerosol processing by cumulus: 2. Evidence for particle nucleation in clouds, submitted to *Journal of Geophysical Research*, 2004) recently suggested in situ particle production in cumulus clouds by comparing the numerical calculations of particle evolution with the observed aerosol concentrations in the marine boundary layer. The relationship of the observed high ultrafine particles to the high cirrus ice crystal surface area is difficult to explain. However, this may suggest some unknown heterogeneous processes related to the cloud surfaces (for example, aqueous reactions on ice surfaces), which can generate nucleation precursors. If the precursor concentrations (such as SO_2 and OH) are very high, particle nucleation is possible even in the case of high surface area. Unfortunately, during CRYSTAL-FACE, in situ measurements of SO_2, OH, H_2SO_4, or NH_3 were not made; these measurements are needed in the future to identify nucleation processes in cirrus clouds.

[19] OH concentrations can be higher near clouds because of the high actinic flux near and above clouds [*Mauldin et al.*, 1999], although within the thin cirrus clouds, enhancement of actinic flux can be minimal. The higher water vapor concentrations near clouds may enhance photochemical production of OH [*Clarke et al.*, 1999]. In addition, there are various processes that produce electricity near and within clouds [*Pruppacher and Klett*, 1997], and recent aircraft studies have indeed measured high average charges on cloud drops [*Beard et al.*, 2004]. If IIN is important for new particle formation in cirrus clouds, cloud electricity can play a substantial role in particle nucleation in clouds.

[20] While some studies used BHN to explain the measured ultrafine particles near marine clouds [*Hegg et al.*, 1990; *Clarke et al.*, 1999], others argue that additional unidentified processes need to be involved [*Hoppel et al.*, 1994]. The UT-LS has high BHN rates because of its lower temperatures. This is also an area where IIN is effective [*Lee et al.*, 2003; *Lovejoy et al.*, 2004]. In addition, various organics and ammonia exist in the tropical/subtropical UT [*Murphy et al.*, 1998], which can contribute via THN. From the current knowledge we think that all these processes contribute to new particle formation in the cirrus clouds. In addition, unknown cloud surface reactions may also be involved, as mentioned above.

[21] It was also very surprising to see that high numbers of ice crystals were observed over an extensive range of RHI, ranging from ~80% to ~160% (e.g., Figure 1). Most observations clearly represent nonequilibrium conditions. Perhaps these conditions were created by waves or mixing of air having different properties during the cirrus formation. Vertical convection may also have played an important role for new particle formation seen in cirrus clouds, similar to the previous suggestions by *Nilsson and Kulmala* [1998] and *de Reus et al.* [1999]. Several days were identified as having been influenced by dust or biomass burning during CRYSTAL-FACE [*Jensen et al.*, 2004], and it is noted that on the days influenced by the biomass burning (e.g., 7 July) or Saharan dust (e.g., 28 July), the RHI ranged from even lower values (<80%) when high IWC was present ($>1.0 \times 10^{-4}$ g m^{-3}). We are currently unable to explain the thermodynamic behavior of these lower RHI in cirrus clouds. A potential cause for the high RHI (~160%) in cirrus clouds has been suggested to be HNO_3 uptake on ice crystal surfaces [*Gao et al.*, 2004]. However, regardless of the different ranges of RHI, it was consistent that the high ultrafine particles coincided with high IWC, suggesting new particle formation in the cirrus clouds.

5. Summary

[22] We have measured high concentrations of ultrafine particles in cirrus clouds. We examined the possibility that ice crystal particles shattered in the sampling inlet and produced these small particles. However, we believe that these observed ultrafine particles were created by in situ new particle formation events in cirrus clouds. We speculate that several possible factors could enhance particle formation in clouds, but at present it is difficult to understand how these new particles form in a condition where very high ice crystal surface areas exist. Cirrus clouds have potential factors favorable for particle formation, including low temperatures, high RHI, high OH production (because of high water vapor), cloud electricity, and atmospheric convection and mixing. However, which factors govern the particle nucleation in clouds in the tropical/subtropical UT or which nucleation processes dominate is an open question.

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B. Anderson, Chemistry and Dynamics Branch, NASA Langley Research Center, MS 483, Hampton, VA 23681, USA.
B. Baker and P. Lawson, SPEC, Inc., 3022 Sterling Cir., Boulder, CO 80301, USA.
D. Baumgardner, Centro de Ciencias de la Atmósfera – UNAM, Universidad Nacional Autónoma de México, Circuito Exterior s/n, Ciudad Universitaria, 04510 México City (D. F.), México.
T. P. Bui and A. Strawa, NASA Ames Research Center, Mail Stop 245-4, Moffett Field, CA 94305-1000, USA.
R. L. Herman, Jet Propulsion Laboratory, MS 183-401,4800 Oak Grove Dr., Pasadena, CA 91109, USA.
G. Kok, Droplet Measurement Technologies, 2400 Central Avenue, Boulder, CO 80301, USA.
B. G. LaFleur, CMDL, National Oceanic and Atmospheric Administration, 325 S. Broadway Street, Boulder, CO 80301, USA.
S.-H. Lee, J. M. Reeves, and J. C. Wilson, Department of Engineering, University of Denver, 2390 S. York Street, Denver, CO 80208-0177, USA. (shanlee@du.edu)
J. V. Pittman and E. M. Weinstock, Engineering and Applied Sciences, Harvard University, 29 Oxford St., Cambridge, MA 02138, USA.